

PATENT SPECIFICATION

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DRAWINGS ATTACHED

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(54) PRODUCTION AND ELECTRODIALYSIS OF HYDROGEN IONS AND HYDROXYL IONS

- (71) We, ASAHI KASEI KOGYO KABUSHIKI KAISHA, a Corporation organised under the laws of Japan, of 25-1, 1-chome, Dojima-hamadori, Kita-ku, Osaka, Japan, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—
- 10 This invention relates to a method for the generation and simultaneous electrodialysis of hydrogen and hydroxyl ions. The method of the invention is particularly suitable for the production of acid and/or alkali from water and water-soluble salts.
- 15 Most prior art methods which involve electrodialysis of hydrogen and hydroxyl ions necessitate the use of bipolar ion exchange membranes to partition the electrolytic cell. Such membranes normally comprise a layer of cation exchange material bonded with a suitable binder to a layer of an anion exchange material. Experience has indicated that these membranes are expensive to manufacture, have a short working life, and do not possess fully satisfactory electrochemical and physical properties.
- 20 The present invention is based on the discovery that the inclusion of a polyelectrolyte assists the dissociation of water and enables stable electrolysis to be carried out over a prolonged period at high efficiency.
- 25 According to the present invention there is provided a method for the generation and simultaneous electrodialysis of hydrogen and hydroxyl ions using a cell having an anode and a cathode and a reaction compartment between the anode and cathode for generating hydrogen and hydroxyl ions by electro-chemical dissociation of water, said reaction compartment being bounded on the anode side by an anion exchange membrane and on the cathode side by a cation exchange membrane, said method comprising introducing into said reaction compartment a dispersion in water of a finely pulverised water-insoluble polyelectrolyte and passing a D.C. current through said cell. The term "polyelectrolyte" as used herein means polymeric material bearing a plurality of positively charged fixed ions, and which does not pass through an ion exchange membrane.
- 30 The method of the present invention is particularly suitable for the production of an acid and/or an alkali from water and a water-soluble salt. In the production of an acid the cell is preferably constructed with an acid compartment (in which the acid accumulates) by arranging a further anion exchange membrane between the reaction compartment and the cathode. The salt solution is introduced on the cathode side of the acid compartment and is preferably partitioned from the catholyte by means of a further cation exchange membrane.
- 35 In the production of an alkali the cell is preferably constructed with an alkali compartment (in which the alkali accumulates) by arranging a further cation exchange membrane between the reaction compartment and the anode. The salt solution, which may be of a alkali metal is introduced on the anode side of the alkali compartment and is preferably partitioned from the anolyte by means of a further anion exchange membrane.
- 40 According to a preferred embodiment of the invention in which acid and alkali is simultaneously produced, the cell comprises a plurality of salt, acid, reaction (in which water dissociation occurs), and alkali compartments in the order specified from the cathode to the anode, said compartments being formed by a plurality of alternate anion and cation exchange membranes, the membrane nearest the cathode being a cation exchange membrane and the membrane nearest the anode being an anion exchange membrane

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The present invention will now be explained in detail with reference to the accompanying drawing, in which:

Figure 1 is a schematic view of one embodiment of an apparatus for carrying out the present invention;

Figure 2 is a graph illustrating the operational characteristics of the apparatus which is used in the Example; and

Figure 3 is a schematic view of a second embodiment of apparatus for carrying out the method of the invention.

Referring to Fig. 1, the apparatus comprises an electrolytic cell which is divided into a plurality of compartments by alternate anion exchange membranes 3 and cation exchange membranes 4. The membranes 3 and 4 are disposed at a predetermined relative separation between a cathode 1 of suitable material (e.g. graphite, iron, nickel, or stainless steel) and an anode 2 of suitable material (e.g. graphite, platinum, titanium, tantalum, or zirconium or a material plated with a noble metal, e.g. platinum). The membranes 3 and 4 are arranged to form a plurality of reaction (or water decomposition) compartments 5, acid compartments 6, alkali compartments 7, and salt compartments 8 in the order 8,6,5,7,8,6,5,7. . . from the cathode towards the anode, i.e., salt compartments 8 and reaction compartments 5 have cation exchange membranes 4 on the cathode sides thereof and anion exchange membranes 3 on the anode sides thereof, while acid compartments 6 and alkali compartments 7 have anion exchange membranes 3 on the cathode sides thereof and cation exchange membranes 4 on the anode sides thereof.

A polyelectrolyte, as an aqueous suspension of a finely pulverised water insoluble polymeric material, is introduced into the reaction compartments 5. Water or an aqueous acidic solution is fed to the acid compartments 6 from a common feed pipe 10, water or an aqueous alkaline solution is fed to the alkali compartments 7 from a common feed pipe 11, and an aqueous solution of organic salt or inorganic salt is fed to the salt compartments 8 from a common feed pipe 12.

A D.C. voltage is applied between the cathode and the anode provided at both ends to pass direct electric current in a direction to allow it to flow from the anion exchange membrane side of the reaction compartment toward the cation exchange membrane side of the reaction compartment in the apparatus.

During the applications of D.C. voltage through the apparatus, the hydrogen ions H^+ and the hydroxyl ions OH^- are generated in the reaction compartment 5, while salt in each of said salt compartments 8 is decomposed into corresponding anions and cations.

The hydrogen ions H^+ thus formed in the reaction compartment 5 travel through the cation exchange membrane 4 forming a partition on the cathode side of the water compartment 5, into the adjacent acid compartment 6 while anions formed in the salt compartment 8 travel through the anion exchange membrane forming a partition on the anode side of the salt compartment by electro dialysis into the adjacent acid compartment whereby an acid is formed in each of the acid compartments.

On the other hand, the hydroxyl ions OH^- formed within the reaction compartment 5 travel through the anion exchange membrane forming a partition on the anode side of the reaction compartment 5 into the adjacent alkali compartment 7 by electro dialysis, while the cations formed within the salt compartment 8 travel through the cation exchange membrane forming a partition on the cathode side of the salt compartment 8 into the adjacent alkali compartment 7, whereby an alkali is formed within each of the alkali compartments 7.

In the meantime, water is consumed in the reaction compartments 5 by passing an electric current due to the decomposition of water and electro dialysis, and thus water must be supplied to the reaction compartments 5 by a suitable means, for example, through a pipe 9 communicating with the reaction compartments 5. Alternatively, the water within the reaction compartments 5 may be circulated between a water circulating tank provided outside the electro dialysis cell and the reaction compartments 5 and an amount of water corresponding to the water loss due to the decomposition and electro dialysis is supplied to the water circulating tank.

The solutions passed through the acid compartments 6, alkali compartments 7 and salt compartments 8 individually are led to the outside of the electro dialysis cell through the respective common discharge pipes 13, 14 and 15 correspondingly.

When a strong acid and a strong base are to be prepared by decomposing an acid-strong base type salt, such as $NaCl$, an electro dialysis cell having such a structure as explained above is necessary, but when a salt of weak acid or weak base is to be decomposed, the structure of the electro dialysis cell can be much simplified.

For example, when sodium acetate is to be decomposed, it is not necessary to inhibit the migration of the hydrogen ions by means of the anion exchange membrane, because the formed acetic acid is a weak acid. Thus only a cation exchange membrane is placed between a reaction compartment and the next reaction compartment, and the anion exchange membrane can be omitted from between said compartments. By carrying out

electrodialysis while an aqueous sodium acetate solution is passed to the compartments which are adjacent to the reaction compartments on the cathode side thereof and receive the hydrogen ions, the salt compartments can serve as the acid compartments at the same time, and acetic acid can be accumulated in the salt compartments.

When a salt of weak base is to be decomposed, the cation exchange membrane is omitted from between each reaction compartment and the next reaction compartment and only an anion exchange membrane is inserted there between, contrary to the decomposition of a salt of weak acid. In these cases, one kind of compartment can be saved, and consequently, one piping system as well as one storage vessel system can be saved.

The concentration of water-insoluble polyelectrolyte in the suspension is usually at least 1% by weight, preferably 5% by weight.

The upper limit of the amount is determined by economic consideration and operational parameters.

Therefore, while the decomposition of water may effectively proceed with a considerable amount of said polyelectrolytes, the use of a greater amount of them is usually not economically attractive.

It can be presumed that water molecules are decomposed, and H^+ and OH^- are generated at the membrane boundary surfaces between the cation exchange membranes 4 constituting one partition wall of the reaction compartments 5 and the aqueous solution or suspension in contact with the membranes.

As said finely pulverized water insoluble polymeric materials capable of forming an electrolyte suspension in water as a medium, finely pulverized anion exchange resins can be used. For example, such anion exchange resins may be pulverized by a ball mill, sand mill, roll mill, attritor mill or other pulverizer to less than several tens of microns, preferably less than several microns. Examples of suitable anion exchange resins are Amberlite IRA-400, IRA-401, IRA-402, IRA-405, IRA-900, IRA-410, IRA-904, IRA-411, IRA-911, and IRA-190, and Diaion SA10A and PA304. The words "Amberlite" and "Diaion" are registered trade marks.

Thus, any inorganic salts and organic salts, in conjunction with hydrogen ions H^+ and hydroxyl ions OH^- , can be converted into corresponding acid and alkali, respectively so long as the salt, and formed ions do not adversely affect the electrodialysis.

Applications of the present method for generating hydrogen ions and hydroxyl ions to industry cover quite a wide field. Production of NaOH and HCl from NaCl, production of CH_3COOH and NaOH from

CH_3COONa , production of NH_4OH and HCl from NH_4Cl , and many other applications can be enumerated, based on the enhanced decomposition of water into hydrogen ions H^+ and hydroxyl ions OH^- by the promoting effect of said electrolyte.

The following Example will illustrate the invention and the manner in which it may be carried into effect:

All the ion exchange membranes used in the following Example are Types CK-1 (cation exchange membrane) and CA-1 (anion exchange membrane) made by Asahi Kasei Kogyo K.K. Japan, which have been prepared from polymeric styrene-divinyl benzene as a matrix, into which sulfonic acid and quaternary ammonium groups respectively have been introduced:

Example.

Anion exchange resins (Diaion PA-304, manufactured by Mitsubishi Kasei K.K. Japan) were pulverized into fine particles in a ball mill for 100 hours, and suspended in water at the rate of 0.5 equivalent exchange capacity per liter.

Measurements of transport numbers and electric potential were made on the thus obtained suspension.

Measurement of transport numbers

The electrodialyzer which was used in this example comprises three compartments, namely, anode, cathode and reaction compartments.

The suspension described above was poured into the reaction compartment whose partitioning anion exchange membrane was fixed toward the anode side and whose partitioning cation exchange membrane was fixed toward the cathode side.

A 0.5N-NaOH aqueous solution was placed in the anode compartment at the outside of the anion exchange membrane of the reaction compartment and a 0.5 N-HCL solution was placed in the cathode compartment at the outside of the cation exchange membrane of the reaction compartment.

A direct electric current was passed at a current density of 3 Amp/dm² through the cell to affect electrodialysis. The transport numbers were measured. That is, the data obtained were that the H^+ (or OH^-) ion transport number was 0.926 (which corresponded to the current efficiency), that the Na^+ ion transport number was 0.041 and that the Cl^- ion transport number was 0.038. The measurement was carried out under a static condition of solutions.

As electrode materials, a platinum anode and a silver chloride cathode were used. Pure water was added into the reaction compartment only to the amount corresponding to the water loss made during the electrodialysis. The effective current passing area was 18 cm² and the membrane distance of the reaction compartment was 0.75 mm.

Measurement of voltage—current relation

The electro dialysis apparatus as described above was employed in this measurement.

The measurement of the voltage was effected
5 by placing an alkaline sodium chloride solution containing NaOH in 0.4N and NaCl in 0.1N in a compartment at the outside of the anion exchange membrane of the reaction
10 compartment, the former solution being isolated from the latter with a cation exchange membrane interposed there between, placing an acidic sodium chloride solution containing HCl in 0.4N and NaCl in 0.1 N in a
15 compartment at the outside of the cation exchange membrane of the reaction compartment, the former solution being isolated from the latter with an anion exchange membrane interposed there between, passing the direct electric current through the cell
20 while allowing these solutions in these compartments to be renewed continuously and measuring a potential difference between silver chloride electrodes provided near the membrane surfaces bounding the reaction
25 compartment by means of a valve potentiometer. The change in voltage with the current density is given in Fig. 2 as a curve 2-(1).

WHAT WE CLAIM IS:

1. A method for the generation and simultaneous electro dialysis of hydrogen and hydroxyl ions using a cell having an anode and a cathode and a reaction compartment between the anode and cathode for generating hydrogen and hydroxyl ions by electro-chemical dissociation of water, said reaction
30 compartment being bounded on the anode side by an anion exchange membrane and on the cathode side by a cation exchange membrane, said method comprising introducing into said reaction compartment a dispersion in water of a finely pulverized water-insoluble polyelectrolyte as herein defined
35 and passing a D.C. current through said cell.

2. A method according to claim 1 for the
45 production of an acid, wherein a further anion exchange membrane is disposed between said reaction compartment and the cathode to form an acid compartment and a salt of the desired acid is introduced on the
50 cathode side of the acid compartment.

3. A method according to claim 2, wherein a further cation exchange membrane is disposed between the acid compartment and

the cathode to form a salt compartment.

4. A method according to any one of the
55 preceding claims for the production of an alkali, wherein a further cation exchange membrane is disposed between said reaction compartment and the anode to form an alkali compartment and a salt of alkali metal
60 is introduced on the anode side of the alkali compartment.

5. A method according to claim 4, wherein a further anion exchange membrane is disposed between the alkali compartment and
65 the anode to form a salt compartment.

6. A method according to any one of the preceding claims for the simultaneous production of acid and alkali in which the cell employed comprises a plurality of salt, acid,
70 reaction and alkali compartments in the order specified from the cathode to the anode, said compartments being formed by a plurality of alternate anion and cation exchange membranes, the membrane nearest
75 the cathode being a cation exchange membrane and the membrane nearest the anode being an anion exchange membrane.

7. A method according to claim 6, wherein water, with said polyelectrolyte, is fed continuously to said reaction compartments, an aqueous salt solution is fed continuously to said salt compartments, water or aqueous acid is fed continuously to said acid
80 compartments and water or aqueous alkali is fed to said alkali compartments, aqueous acid and aqueous alkali being withdrawn respectively from said acid and alkali compartments.
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8. A method according to any one of
90 claims 1 to 7, wherein said polyelectrolyte is an anion exchange resin in particulate form.

9. A method according to any one of the preceding claims, wherein said polyelectrolyte is present in the dispersion in an amount
95 of at least 1% by weight.

10. A method for the generation and simultaneous electro dialysis of hydrogen and hydroxyl ions substantially as described with reference to the Example.
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COMPLETE SPECIFICATION

3 SHEETS

This drawing is a reproduction of
the Original on a reduced scale.

SHEET 1

Fig. 1

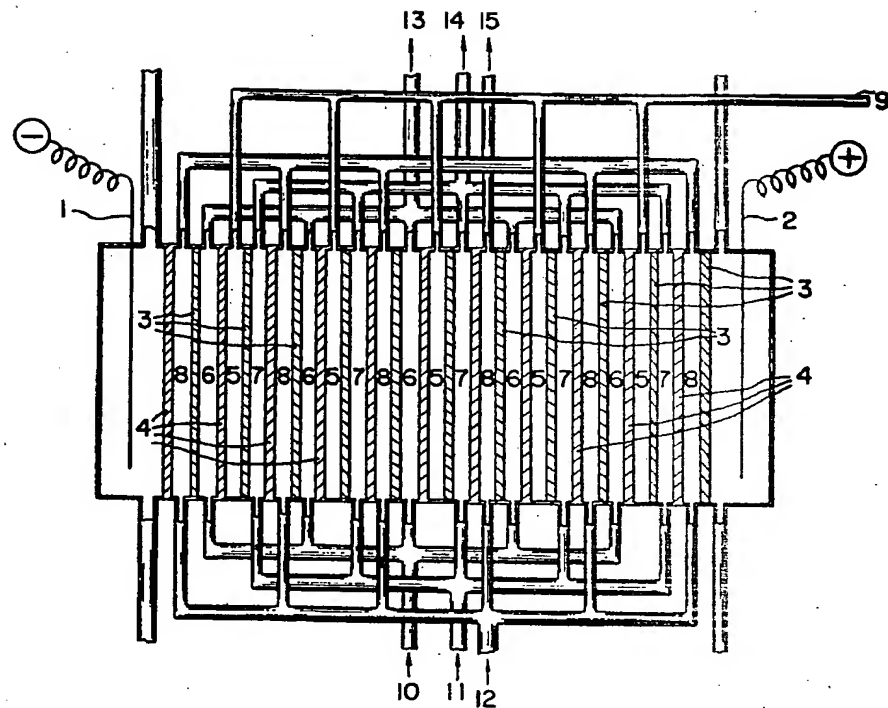


Fig. 2

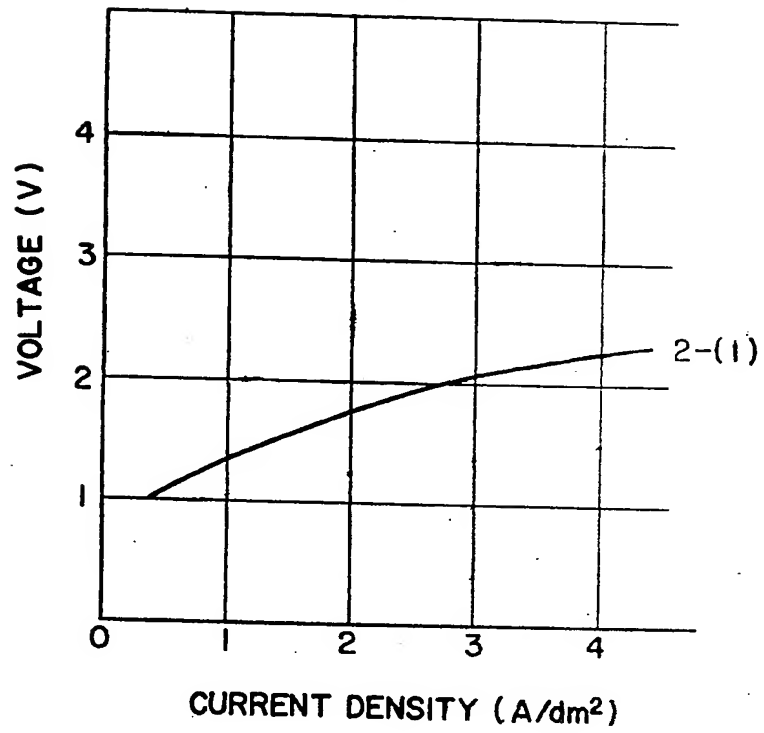


Fig. 3

